Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes

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HIGHLIGHTS

- Fly ash was identified as a route of POPs release from the coking industry.
- Emission factors were derived for unintentionally produced POPs in coking ash.
- The data obtained were useful for developing an integrated source inventory.
- Congener profiles for the unintentionally produced POPs in coking ash are presented.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 20 April 2013

Received in revised form 12 July 2013

Accepted 29 July 2013

Available online 4 August 2013

Keywords:

Dioxins

Polychlorinated biphenyls

Polychlorinated naphthalenes

Coking process

Fly ash

ABSTRACT

The coking process has been found to be an important source of unintentionally produced persistent organic pollutants (UP-POPs). However, the concentrations, profiles, and emission factors of UP-POPs in fly ash from coke plants have not been studied. In this study, six UP-POPs (polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz)) were identified and quantified in fly ash from eight coke plants. The average concentrations of the PCDDs, PCDFs, and “dioxin-like” PCBs were 1.5, 2.26, and 0.26 pg TEQ g⁻¹, respectively, and the average concentrations of the PCNs, HxCBz, and PeCBz were 256, 290, and 146 pg g⁻¹, respectively. The proportion each homolog contributed to the total concentration of the PCDFs, PCBs, and PCNs decreased with increasing chlorination level. The PCDFs contributed the biggest proportion of the total UP-POPs toxic equivalents (TEQs), and the average emission factors in fly ash were 10.5, 17.3, and 1.82 ng TEQ t⁻¹ for the PCDDs, PCDFs, and “dioxin-like” PCBs, respectively, and 1792, 2028, and 1025 ng t⁻¹ for the PCNs, HxCBz, and PeCBz, respectively. These data are essential for establishing an integrated UP-POP release inventory.

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1. Introduction

Since the discovery of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in flue gases and fly ash from municipal solid waste incinerators in 1977 [1],

the formation and emission of PCDDs and PCDFs (PCDD/Fs) and other “dioxin-like” (dl-) compounds has attracted increasing concern because of their adverse effects on the environment and human health [2–6]. Other dl-compounds, such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz), can also be unintentionally produced and released during thermal processes [7,8], and these chemicals (including the PCDD/Fs) are called unintentionally produced persistent organic pollutants

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Table 1
Basic information on the coke plants studied.

Site name	P1	P2	P3	P4	P5	P6	P7	P8
Height of ovens (m)	6	6	7.3	4.3	4.3	6	4.3	4.3
Annual capacity (million ton)	0.5	1.8	2.2	0.6	1	1	0.96	0.7
Coal charging technique	TC ^a	TC	TC	TC	SC ^b	TC	SC	TC
Coke quenching method	Water	Nitrogen	Nitrogen	Water	Water	Water	Water	Water
APCD ^c	BFs ^d	BFs	BFs	BFs	BFs	BFs	BFs	BFs
Origin of fly ash	PC ^e , CC	PC ^f , CC; QC ^g	PC;	PC	PC; CC	PC; CC	PC	CC; PC
Amount of fly ash produced for per ton of coke production (kg t ⁻¹)	7	6	5	9	9	6	10	7

^a Top charging.

^b Stamp charging.

^c Air pollution control device.

^d Bag filters.

^e The ash was collected during the pushing of the coke.

^f The ash was collected during the charging of the coal.

^g The ash was collected during the quenching of the coke.

(UP-POPs) [9]. Identifying and quantifying UP-POPs in various anthropogenic sources is the primary step in controlling their emission and reducing the environmental burden of, and human exposure to, these compounds [10,11].

Stack gas and residue emissions are the two main ways UP-POPs are released from industries that have major thermal processes. Heterogeneous reactions during thermal processes are the dominant UP-POP formation mechanisms [12], and fly ash is considered to be an important matrix for catalyzing these heterogeneous reactions because it contains relatively large amounts of carbon and catalytic elements [13–16]. High UP-POPs concentrations have been found in fly ash samples from various thermal industries, so fly ash is considered to be one of the most important sources of UP-POPs to the environment [17].

It has been speculated that the coking process is a potential source of UP-POPs, because it has conditions that are essential for UP-POP formation, including macromolecular materials in coal (the carbon source), chlorine (inorganic or organic), catalytic metal elements in the raw materials, and suitable temperature ranges. We have confirmed that the coking process is a potential source of UP-POPs by characterizing stack gas emissions from coking plants in previous studies [9,10]. However, concentrations, profiles, and emission factors of UP-POPs in fly ash from coking plants have not been reported up to now, and these are essential for developing an integrated UP-POP release inventory for the coking industry.

In this study, we collected fly ash samples from eight coke plants in China, and determined six types of UP-POPs in the samples using isotope dilution gas chromatography-mass spectrometry. The primary aims of the study were: (1) to quantify the concentrations of UP-POPs in fly ash samples from coking processes, to understand the release of UP-POPs in coking ash; (2) to assess the UP-POP profiles in fly ash, which could help understand the UP-POP formation mechanisms and identify specific sources; and (3) to derive emission factors for UP-POPs in fly ash, so that an integrated UP-POP release inventory for the coking industry can be developed. To the best of our knowledge, this is the first intensive investigation of the concentrations, profiles, and emission factors of UP-POPs in fly ash from the coking industry. Because of the scale of industrial activity in China, the UP-POP emission data for typical Chinese coke plants produced from this study might have significant implications for evaluating UP-POP emissions from the global coking industry.

2. Experimental

2.1. Sampling and information on the coke plants studied

Coke is produced by carbonizing coal in an oven that is externally heated to approximately 1000 °C in the absence of air. The

coke is removed from the oven and quenched with water or dry inert gas. The formation and emission of UP-POPs can occur during three different stages of the process, including charging the coal (CC), pushing the coke (PC), and quenching the coke (QC). The coke production process has been described in detail previously [9], and a schematic of the coking process is presented in the Supplementary Material (Fig. S1). In this study, UP-POPs were analyzed in fly ash emitted from eight coke plants that were of different sizes and that used different operational techniques. The height of the coke ovens in the plants ranged from 4.3 to 7.3 m, and the coke plants used either top charging or stamp charging of coal, and either water quenching or inert gas quenching of the coke. Samples of the fly ash produced during the CC, PC, and QC processes were collected separately, from the fabric bag filters used to clean the emissions. The origins (CC, PC, or QC) of the fly ash collected are given in Table 1. The fly ash samples were collected using a stainless steel spoon. Each composite fly ash sample comprised 3–6 sub-samples from the chosen sampling points. The fly ash samples were tightly wrapped in aluminum foil and sealed in polyethylene (PE) bags to avoid contamination and loss. The samples were stored in a refrigerator until analysis. Detailed information on the coke plants studied and on the fly ash samples collected is given in Table 1.

2.2. Chemical analysis

PCDDs, PCDFs, and PCBs were analyzed by isotope dilution high resolution gas chromatography-high resolution mass spectrometry (HRGC/HRMS), using modified US Environmental Protection Agency (EPA) methods 8290 (PCDD/Fs) and 1668A (PCBs). The detailed sample extraction, cleanup, and instrumental analysis procedures for the PCDD/Fs and dl-PCBs have been described in detail by Ba et al. [17]. Briefly, the fly ash samples were spiked with known amounts of ¹³C₁₂-labeled PCDD, PCDF, and PCB internal standards, treated with 1 mol L⁻¹ HCl, then Soxhlet extracted with 250 mL of toluene for about 24 h. The extracts were concentrated in a rotary evaporator, then subjected to a series of cleanup steps, including columns containing silica gel treated with 44% (by weight) sulfuric acid and multilayer silica gel columns. PCDDs, PCDFs, and PCBs were then fractionated using basic alumina columns, each of the fractions was reduced to about 20 µL by rotary evaporation and under a gentle stream of nitrogen, and ¹³C₁₂-labeled PCDD, PCDF, and PCB injection standards were added.

PCNs were analyzed using an isotope dilution HRGC/HRMS method that has been described previously [10,18]. Briefly, the samples were spiked with known amounts of ¹³C₁₀-labeled PCN internal standards (catalog no. ECN-5102, containing ¹³C₁₀-PCNs-27, -42, -52, -67, -73, and -75; Cambridge Isotope Laboratories, Andover, MA, USA). The samples were Soxhlet extracted and the

Fig. 1. Concentrations (A, pg g^{-1}) and TEQs (B, pg TEQ g^{-1}) of the UP-POPs investigated.

cleanup was the same as for the PCBs. The final extracts were reduced to about $20 \mu\text{L}$ and a $^{13}\text{C}_{10}$ -labeled PCN-64 injection standard (catalog no. ECN-5260; Cambridge Isotope Laboratories) was added.

The PCDD, PCDF, PCB, and PCN congeners were identified and quantified using an HRGC/HRMS instrument, monitoring two ions for each analyte. Separation was achieved using a DB-5ms fused silica column (60 m long, 0.25 mm i.d. , $0.25 \mu\text{m}$ film thickness; J&W, Agilent Technologies Inc., Santa Clara, CA, USA). The HRMS instrument was operated at around 10,000 resolution, in selected ion monitoring mode.

For the analysis of HxCBz and PeCBz, the samples were spiked with known amounts of $^{13}\text{C}_6$ -labeled polychlorinated benzenes (PCBzs) (catalog no. EM-1725-A; Cambridge Isotope Laboratories), including $^{13}\text{C}_6$ -HxCBz and $^{13}\text{C}_6$ -PeCBz, extracted, and then purified using multilayer silica gel columns. The extracts were then analyzed for HxCBz and PeCBz using an Agilent 6890 GC (Agilent Technologies Inc.) equipped with a DB-5ms capillary column (30 m long, 0.25 mm i.d. , $0.25 \mu\text{m}$ film thickness; J&W) interfaced with an Agilent 5973 N MSD. HxCBz and PeCBz were quantified using $^{13}\text{C}_6$ -HxCBz and $^{13}\text{C}_6$ -PeCBz as isotope dilution internal standards.

2.3. Quality assurance and quality control

To identify a particular analyte, its retention time had to be within 2 s of the retention time of the equivalent internal standard and the ratio between the monitored ions for the analyte had to be within 15% of the theoretical value. The recoveries were 39–82% for the $^{13}\text{C}_{12}$ -labeled PCDD/Fs and 42–138% for the $^{13}\text{C}_{12}$ -labeled PCBs, which met the requirements of US EPA methods 8290 and 1668A. The recoveries of the $^{13}\text{C}_{10}$ -labeled PCNs were 36–125% and the recoveries of $^{13}\text{C}_6$ -HxCBz and $^{13}\text{C}_6$ -PeCBz were 34–72%. Laboratory method blank samples were included with each sample batch analyzed, and octachlorodibenzo-*p*-dioxin (OCDD), octachlorodibenzofuran (OCDF), PCB-28, PCN-1, and PCN-2 were found in the blanks at concentrations above their LODs but at much lower than 10% of the concentrations found in samples. The analytical laboratory had participated in a number of international PCDD, PCDF, and PCB intercalibration studies, using fly ash from waste incinerators, organized by the UNEP, Intercal AB (Sweden), and the Norwegian Institute of Public Health. The laboratory generally performed at an acceptable level in these intercalibration studies, and, for example, the *z*-scores for the laboratory in the 13th round of the international intercalibration study were within

the range $-1 < z\text{-scores} < +1$ for the PCDD, PCDF and dl-PCB toxic equivalents (TEQs) in fly ash samples from waste incinerators.

3. Results and discussion

3.1. Concentrations of UP-POPs in fly ash samples

The concentrations and TEQs of selected UP-POPs in the fly ash samples analyzed are presented in Fig. 1. WHO-TEF values published by van den Berg et al. [19] were used to calculate the PCDD, PCDF, and dl-PCB TEQs, and the PCN and HxCBz TEQs were calculated using the TEFs reported by Noma et al. [20] and van Birgelen et al. [21], respectively. The average concentrations found were 54.7 pg g^{-1} ($1.50 \text{ pg TEQ g}^{-1}$) for the PCDDs, 99.6 pg g^{-1} ($2.26 \text{ pg TEQ g}^{-1}$) for the PCDFs, 266.3 pg g^{-1} ($0.26 \text{ pg TEQ g}^{-1}$) for the dl-PCBs, 256 pg g^{-1} ($0.14 \text{ pg TEQ g}^{-1}$) for the PCNs, 290 pg g^{-1} ($0.03 \text{ pg TEQ g}^{-1}$) for HxCBz, and 146 pg g^{-1} for PeCBz. However, fly ash from the QC process of only one plant was analyzed for UP-POPs, so the uncertainties involved in estimating UP-POP emission concentrations in QC fly ash for the whole coking industry from this sample are likely to be large. However, the QC process is not, at the moment, commonly used in the coking industry, so the effect this uncertainty will have on the emission estimates for the coking industry as a whole will not be very important.

It can be seen from Fig. 1 that the concentrations of the six types of UP-POPs that were analyzed in the fly ash samples decreased in the order PCBzs > PCNs > dl-PCBs > PCDFs > PCDDs, but that the TEQs decreased in the order PCDFs > PCDDs > dl-PCBs > PCNs > HxCBz. The concentration order PCBzs > PCDFs > PCDDs > PCBs normally indicates de novo synthesis [22]. The PCDF to PCDD ratio ($R_{\text{DF/DD}}$) has been used to identify the dominant formation mechanism(s) in a system, and many studies have shown that PCDD/Fs formed from precursors have $R_{\text{DF/DD}}$ values much lower than one, but that de novo synthesis normally gives $R_{\text{DF/DD}}$ values greater than one [9,23]. From Fig. 1, it can be seen that the PCDFs were present at much higher concentrations than the PCDDs, suggesting that they were predominantly formed by de novo synthesis during the coking processes.

To our knowledge, this study is the first time six UP-POPs have been intensively monitored in fly ash samples from coking plants, and no other data on UP-POPs in coking ash appear to be available for comparison. Waste incineration and metal smelting have been considered to be major sources of UP-POPs emissions from industries that use thermal processes. Thus, to assess which sources

Fig. 2. PCDD, PCDF, PCB, and PCN homolog profiles in the fly ash samples.

should be considered as priorities for decreasing the release of UP-POPs, the UP-POP concentrations we found in fly ash from coking processes were compared with the concentrations found in fly ash from waste incinerators and metallurgical plants (Fig. S2 in the Supplementary Material). The UP-POP concentrations were far lower in fly ash from the coking processes than from the waste incineration and metallurgical fly ash. The elemental compositions of the raw material and the fly ash are very important in the formation of UP-POPs [13,24], and the effect of chlorine and sulfur on PCDD/F formation has been investigated in many studies [25,26]. The ratio of sulfur to chlorine ($R_{S/Cl}$) normally correlates with the PCDD/F concentrations formed, with a low ratio indicating a high chlorine content, which can promote PCDD/F formation, and a low sulfur content, which inhibits PCDD/F formation. The municipal solid waste $R_{S/Cl}$ is about 1:3, and the $R_{S/Cl}$ for coal used for coking is about 5:1. Therefore, the high sulfur content of the coking coal could cause relatively little formation of UP-POPs, by inhibiting the Deacon reaction that is responsible for catalyzing the formation of molecular chlorine during de novo synthesis. The Deacon reaction and the inhibiting reaction are shown in Eqs. (3) and (4). Secondary copper and secondary aluminum smelting systems normally have much higher chlorine contents than other processes, because PVC and other organic materials are present in the wastes that are used as raw materials. Copper and aluminum are also able to catalyze the formation of UP-POPs, so more UP-POPs are normally formed during secondary metal smelting than in other thermal processes.

3.2. UP-POP profiles in fly ash samples

The UP-POP homolog profiles in the fly ash samples are shown in Fig. 2. The proportion each PCDF, PCB, and PCN homolog contributed to the total concentration decreased with increasing number of chlorines. Chlorination has been shown to be one of the most important formation mechanisms for the PCDFs, PCBs, and PCNs during waste incineration [27]. Our homolog profiles suggested that chlorination might also be an important pathway for the formation of PCDFs, PCBs, and PCNs during the coking processes,

Fig. 3. PCDD/F congener profiles in the fly ash samples.

but different trends were observed for the PCDDs, indicating that the PCDD formation mechanism might be different from that of the PCDFs, PCBs, and PCNs. The homolog profiles for the three different processes (CC, PC, and QC) were very similar, indicating that similar formation mechanisms occurred in the different process for the UP-POPs investigated.

The congener profiles of the 17 2,3,7,8-substituted PCDD/Fs and the 12 dl-PCBs were used as signatures for the PCDD/Fs and dl-PCBs in the fly ash from the coking processes. To evaluate similarities and differences in the PCDD/F and dl-PCB patterns, the individual PCDD/F and dl-PCB congener concentrations were normalized to the sum of the 2,3,7,8-substituted PCDD/F concentrations and the sum of the dl-PCB concentrations, respectively. The PCDD/F and dl-PCB congener profiles are shown in Figs. 3 and 4, respectively. It can be seen that 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, OCDD, 1,2,3,4,6,7,8-heptachlorodibenzofuran, and OCDF were the dominant contributors to the sum of the 2,3,7,8-substituted PCDD/Fs. PCBs-118, -105, and -77 were the top three dl-PCB congeners. The PCDD/F and dl-PCB congener profiles were very similar in ash from each of the three coking processes (PC, CC, and QC). Strong similarities have also been seen in the PCDD/F and dl-PCB congener profiles of fly ash and stack gas emissions [9].

The concentration of each PCN congener was expressed as a fraction of the corresponding homolog concentration, to create the PCN congener profiles shown in Fig. 5. This normalization method minimizes the influence of the concentrations of different PCN homologs and allows the congener profiles to be compared more easily [28,29]. The CN-1 fractions were slightly higher than the CN-2 fractions for all three coking processes, and this is similar to what has been found for waste incinerators. However, the CN-1

Fig. 4. dl-PCB congener profiles in the fly ash samples.

Fig. 5. PCN congener profiles (relative to the concentrations of the corresponding homologs) in the fly ash samples.

Table 2

Emission factors derived for the UP-POPs investigated in fly ash samples from coking processes.

UP-POPs	Num. of samples	Mass emission factor (ng t ⁻¹)						TEQ emission factor (ng TEQ t ⁻¹)					
		Minimum	Maximum	Median	Mean	SD ^a	Geometric mean	Minimum	Maximum	Median	Mean	SD ^a	Geometric mean
PCDFs	14	84	2436	520	768	592	527	1.11	53.9	13.2	17.3	3.0	11.4
PCDDs	14	125	997	276	383	274	316	1.59	41.0	8.52	10.5	1.6	7.21
dl-PCBs	14	210	13,597	587	1864	3599	780	0.07	6.10	1.15	1.82	0.4	1.00
PCNs	14	386	4774	1561	1792	1195	1443	0.15	3.80	0.68	0.97	0.2	0.69
HxCBz	14	264	4536	1919	2028	1553	1352	0.03	0.45	0.19	0.20	0.04	0.14
PeCBz	14	165	2754	628	1025	899	674	–	–	–	–	–	–

^a Standard deviation.

fraction was much higher than the CN-2 fraction in technical PCN mixtures, including the Halowax mixtures [30]. The PCN congeners CNs-66/67 have been identified as indicators of combustion sources [31], and in this study we found that CNs-66/67 were dominant contributors to the hexa-CN homologs, suggesting that CNs-66/67 are also indicators of PCNs created in coking processes. The CN-73 to CN-74 ratio has been found to be important for differentiating PCN sources, and in this study this ratio was about 4:1 in the fly ash samples from the coking processes, in contrast to ratios much lower than ones that have been found for Halowaxes [20]. Generally speaking, the profiles indicated that the PCN congener profiles in fly ash from coking processes are, to some extent, similar to the profiles from waste incineration, but very different from the profiles in technical PCN mixtures. The congener profiles in the fly ash samples will provide more detailed fingerprints for use in PCN source apportionment studies.

3.3. UP-POPs emission factors in fly ash from coking processes

Emission factors are useful for estimating pollutant emissions from whole industries based on limited data. The release of ash residues is an important route of UP-POP release, in addition to stack gas emissions. Although we have published UP-POP emission factors to air from coking processes previously [9,10], UP-POP emission factors in fly ash from coking processes, which are essential for developing a complete inventory, have not been available until now. We investigated the amounts of fly ash produced during the coking processes, so that emission factors for the UP-POPs in fly ash could be derived, and, on average, 7 kg of fly ash was produced

per ton of coke produced (with a range of 5–10 kg per ton of coke produced). The UP-POP emission factors for fly ash were calculated using Eq. (5).

$$\begin{aligned} \text{Emission factor (ng t}^{-1}\text{)} \\ &= \text{concentration (pg g}^{-1}\text{)} \\ &\times \text{amount of fly ash per ton of coke produced (kg t}^{-1}\text{)} \end{aligned} \quad (5)$$

The data ranges, averages, medians, and geometric means of the calculated UP-POP emission factors are shown in Table 2, and it can be seen that the average fly ash emission factors were 10.5, 17.3, and 1.82 ng TEQ t⁻¹ for the PCDDs, PCDFs, and dl-PCBs, respectively, and 1792, 2028, and 1025 ng t⁻¹ for the PCNs, HxCBz, and PeCBz, respectively. Emission factors for PCDDs, PCDFs, and other dl-compounds in coke production residues are not available in the “Standardized toolkit for identification and quantification of dioxin and furan releases” prepared by UNEP [32], so the data from this study will be useful in updating this UNEP “toolkit”. These data will also be useful for developing an integrated UP-POP release inventory for the coking industry.

4. Conclusions

We investigated eight typical coke plants of different sizes that used different techniques to estimate and characterize the emissions of UP-POPs in fly ash from the coking industry. The UP-POP concentrations in the fly ash samples collected from the coking plants were relatively low compared with concentrations reported in fly ash from waste incinerators and secondary nonferrous

smelting plants. Of the UP-POPs investigated, PCDFs were the dominant contributors to the total TEQ values. The PCN congener profiles in the fly ash from the coking processes were similar, to an extent, to those from waste incineration and other thermal processes, but were clearly different from the congener profiles in technical PCN mixtures, and this information will improve the PCN fingerprint database for PCN source identification. We calculated UP-POP emission factors for fly ash, and these will be useful for developing an integrated UP-POP release inventory for the coking industry.

Acknowledgments

We gratefully acknowledge the support from the National 973 Program (No. 2009CB421606), the Hong Kong Scholars Program (XJ2012055), and the National Natural Science Foundation of China (Nos. 21107123 and 21037003).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.07.063>.

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